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"Towards the Assembly and Characterization of Individual Molecules by Use of the Scanning Tunneling Microscope as a Nanoscopic Tool"

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Abstract

This final report details the development and setup of a scanning tunneling microscope (STM) capable of operation at cryogenic temperatures in ultra-high vacuum. Main features of the instrument are rapid cooling of the sample to temperatures below 10K, low electronic and vibrational noise during operation at low temperatures and very good drift stability. These are required prerequisites for the anticipated experiments involving STM controlled molecular synthesis. Initial results are demonstrated.

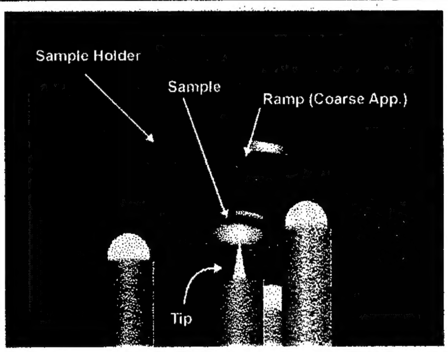
Outline

The setup of the system involved:

- the manufacture of the STM itself and its thermally insulating enclosure,
- the manufacture and set-up of the vacuum system,
- the development of the control electronic,
- the adaptation of a control software and
- final tests and initial results.

This report will detail the most important aspects of these steps in the indicated order. Detailed information on any step is available upon request. This includes e.g. technical drawings, circuit simulation protocols etc.

Design and Setup of the STM

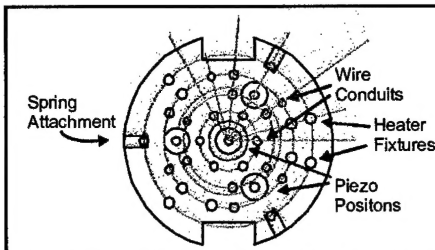


3D View of the sample on the scanner. Coarse approach of the tip (white triangle) to the sample (orange disk) is accomplished by rotational stick-and-slip motion of the three support piezos (blue rods with white spheres) along the red arrow, thereby moving down the ramps cut into the lower side of the sample holder.

The STM is designed according to the well-proven Besocke beetle scheme. Three piezoelectric tube scanners with a diameter of ¼" (Staveley Sensors) are mounted in a triangle, in whose center a forth, similar piezoelectric scanner is placed. The outer three piezos carry the sample holder via aluminum spheres supported from a ceramic mount (left). The center piezo bears the STM tip (usually tungsten wire) in a removable tip holder made from the socket of a pin of an integrated circuit (Amphenol). This socket itself is inserted into a second, slightly larger one. The latter is mounted in a ceramic holder which is attached to the center piezo. The symmetry of this setup minimizes internal temperature drift: any slowly occurring temperature changes will effect the support for the tip and the sample in the same way by which means both effects cancel each other out.

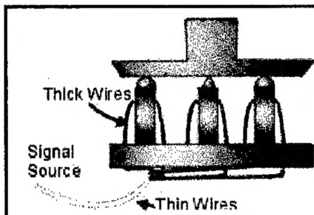
The bottom part of the sample holder, i.e. where it is supported by the aluminum balls of the three outer piezos, is cut into a spiral with three segments. For coarse approach of the sample to the STM tip, the sample holder is rotated down the spiral in a stick-and-slip fashion by use of the three support piezos. For imaging, the support piezos are employed for x and y scanning. This leaves only the fine adjustment of the tip height to the center piezo. In this configuration its outer four electrodes are supplied with the same signal and the center electrode is grounded. The latter provides for excellent electric shielding of the tip thereby reducing the risk of cross-talk between the control signals and the tunneling current. Also the likelihood of interference between the signals for different movement directions is reduced.

The four tube scanners are mounted to a base plate. Both the sample holder and the base plate are manufactured form bulk molybdenum. Using the same material for both scanner plate and sample holder ensures intrinsic thermal compensation. Additionally, molybdenum is refractory enough to allow for heating of the whole sample holder to more than 1200C, enough to prepare silicon and tungsten samples. The material was taken from a rod (Thermoshield) rather than from a plate to avoid a layered internal structure of the molybdenum resulting in significant problems with chipping of the material during manufacture.



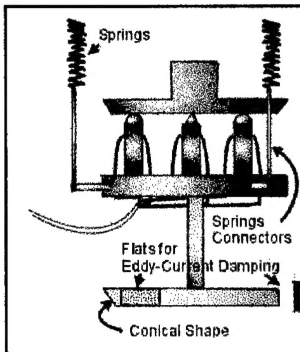
Scanner plate: two of the four positions of the piezos tubes are indicated. Numerous holes connect electric contacts to its bottom side. The reliefs at the top and bottom provide direct access to the tip/sample region for gas/dispersion deposition.

All piezotubes are contacted with capton-insulated copper wire (California Fine Wire) using as adhesive a silver epoxy (Epoxy Technology) specially designed for vacuum applications in microprocessor assembly. Numerous holes are cut into the scanner base plate to feed the connecting wires through to its bottom side. Connections to thinner wires are made using Copper Beryllium contact springs. The thin wires (0.05 mm Cu, capton insulated, Cal. Fine Wire) connect the vibrationally isolated STM to the outside.



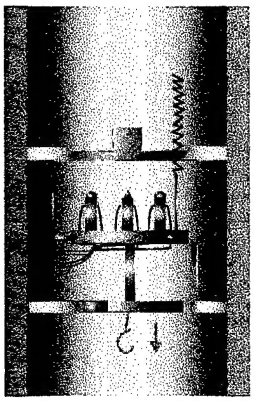
Routing of the electric connections from their contact at the top of the piezo tubes to the cryostat. Red lines indicate thick wires, yellow ones thin wires.

In addition to the connection holes, relieves are cut into the base plate providing access for optical control of the coarse approach process and for adsorption of sample molecules before and during measurements. The temperature of the scanner assembly is measured by a silicon diode (Omega).



The STM is suspended by springs for vibrational insulation. The lower plate has three flat areas for eddy current damping of spring oscillations.

The whole scanner portion is suspended from three springs for vibrational insulation. On the bottom of the base plate another plate is attached at about 1.5" distance. On its round circumference it has six flat of which three are used for eddy current damping with CoSm magnets (Magnetic Materials Inc.) supported on the cryostat.

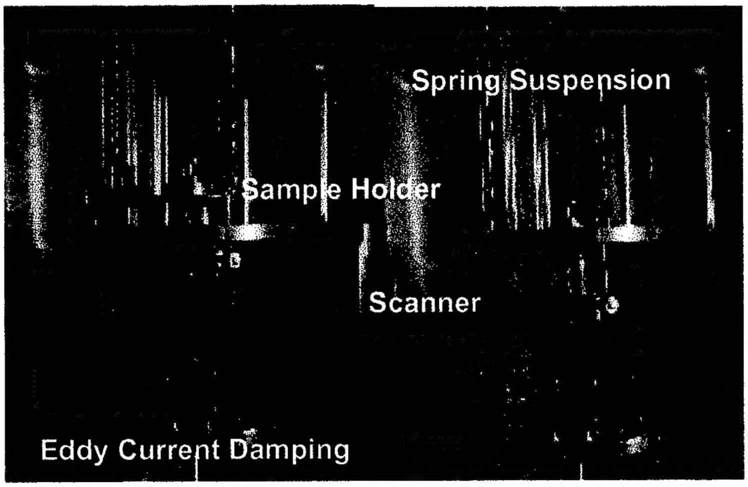


For cool-down and sample exchange the STM is pulled down by a hook attached to its bottom side. This disconnects the scanner from the sample allowing for individual thermal contact to the cryoshield. Good contact is ensured by a conic shape of the contact surfaces.

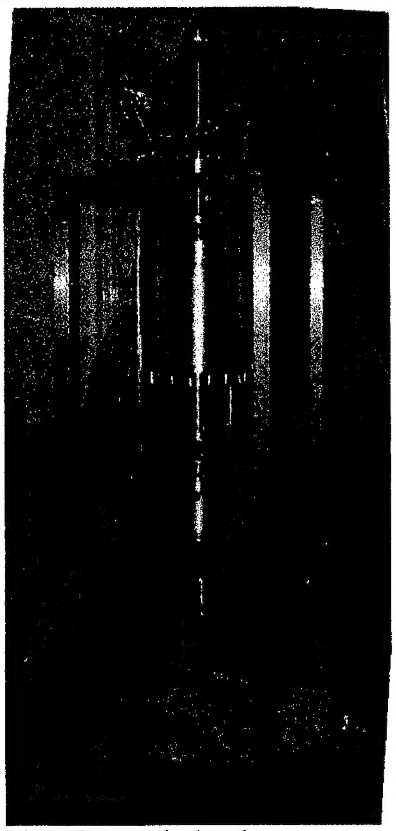
In order to cool the STM rapidly to its operation temperature the whole STM assembly can be pulled down by a hook attached to its bottom plate. Then the sample holder rests with its tapered edge in a conical relief directly connected to the cryoshield. Similarly, the lower plate of the STM is pulled into a conical relief allowing for efficient cooling via its edge, which is tapered wherever no vertical edge is necessary for efficient eddy current damping. Using polished surfaces and exactly matching angles excellent thermal contact is created, which permits rapid cool-down of the sample and the microscope separately.

The retracted position is also the position where sample exchange is performed. Here it is very convenient that the fragile piezotubes are withdrawn from the sample area preventing their damage during sample manipulation. It also reduces the thermal load on the piezo tubes, which would occur if a warm sample were placed upon them. This eliminates an important source of instrument drift.

The whole STM is housed in a split cryogenic shield made of oxygen free copper (rods supplied by Sequoia Copper and Brass, bored and split in-house). It is attached to a liquid helium cryostat (Advanced Research Systems) for rapid cool down. The STM is supported from springs that are attached to the top part of the cryoshield. The support plates for cooling of the sample and the scanner are made from the same copper material and attach directly to the cryoshield thus ensuring efficient thermal contact. ¼" copper tubes (Sequoia Copper and Brass) run on the side of the cryoshield along its long axis. These shield the electric connections to the STM. Multiple-bore ceramic rods separate the cables inside them. This rigid construction provides better shielding at lower capacitance compared to twisted-pair and wire-mesh shielding. This is important to prevent oscillatory behavior of the feedback loop.

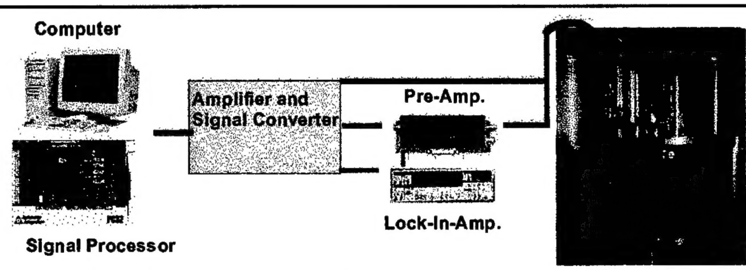


Center portion of the STM within two radiation shields. On the left in scanning position and on the right in sample exchange position.


The STM attached to the cryostat and the flange of the vacuum chamber. Front portion of outer shield is removed to allow optical access.

The inner cryoshield supporting the STM is enclosed in a second shield cooled to an intermediate temperature by the transfer tube shield flow. This cryoshield is similarly bored from a rod of oxygen free copper and split into two parts for instrument assembly (the core actually is the material used for the inner shield). Both

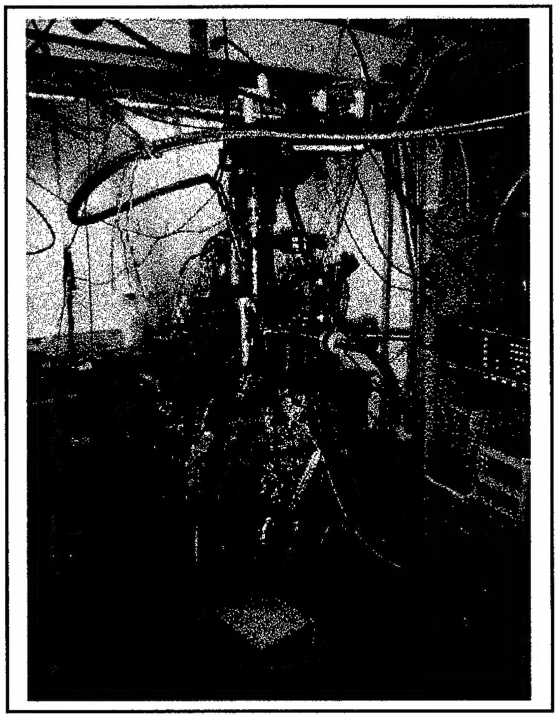
cryoshields have sapphire windows (Castec) allowing optical access to the sample/tip region. Sapphire is chosen because of its thermal conductivity reducing its thermal radiation at low temperatures. Small holes allow the deposition of adsorbates from the outside. Shutter rings are attached on both cryoshields, by which means all (including optical) access to the inside of the cryostat can be blocked. This reduces the thermal load on the STM, decreases the minimum attainable temperature and saves coolant. The cryoshields are electrochemical gold plated (EPSI) after manufacture in order to minimize their thermal radiation.



Connection diagram of the STM setup: a standard PC equipped with a digital signal processor card (DSP) generates the analog control signals for STM operation (scanning, bias etc.) and converts the resultant gap current and lock-in output into a digital signal. A home-built amplifier and signal converter (ASC) box ensures proper ground separation and creates auxiliary signals from the DSP output. It is controlled by numerous digital control signals also generated by the DSP. Amplification of the piezo signals is also provided by the ASC. The tunneling current is amplified by a pre-amp and brought to the DSP via the ASC. A lock-in-amp is used to obtain derivative signals.

The current signal is pre-amplified right outside the STM chamber using a commercial preamplifier (Femto) with software controllable gain (10^8 V/A to 10^9 V/A for imaging, 10^6 V/A to 10^8 V/A for manipulation). Its bandwidth can be set remotely in order to minimize noise while providing sufficient bandwidth for signal modulations which are necessary in dI/dV (d^2I/dV^2) spectroscopy. A lock-in amplifier (Stanford Research Systems) is used to generate a modulation voltage, which controls the bias via respective circuitry in the amplifier and signal converter box (next section). By this modulation the lock-in amplifier is able to measure the derivative of the tunneling current directly.

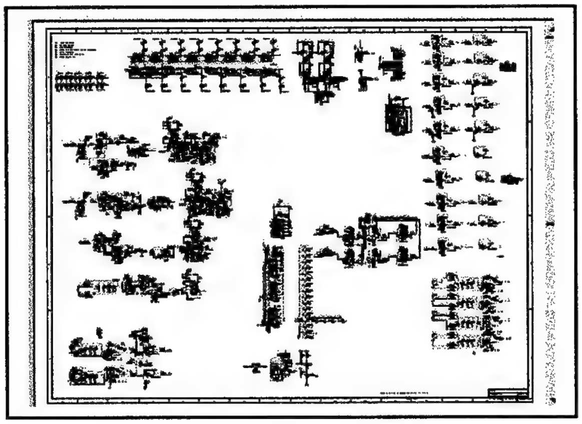
Vacuum Chamber

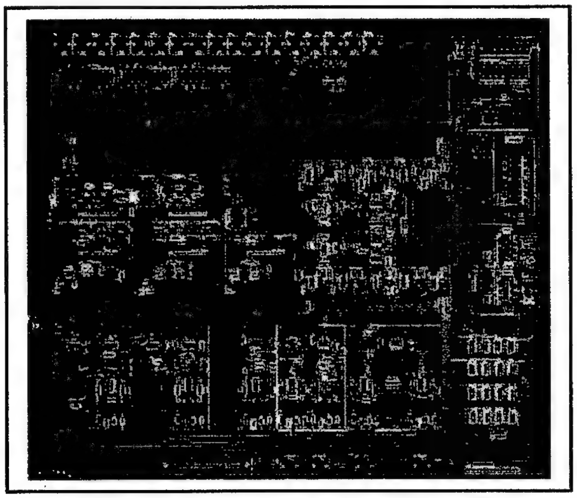


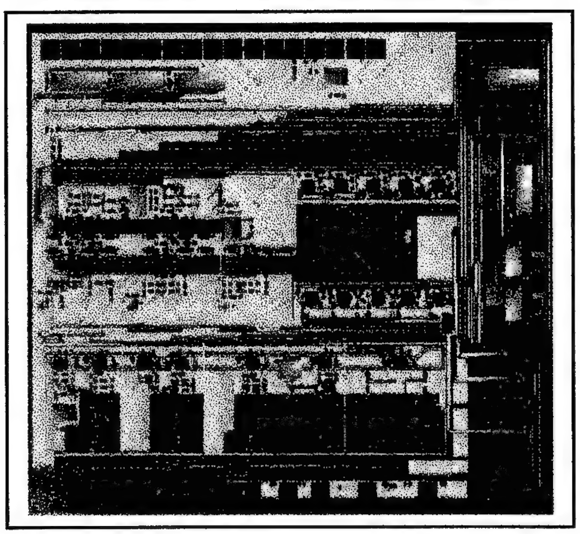
The vacuum chamber itself was manufactured in house from used components. It has an ion pump at the bottom. The STM is inserted by a custom crane from the top. Additional pumping is achieved by a Varian Navigator 551 Turbo pump and a Titanium Sublimation Pump. Apart from standard vacuum instrumentation (ion gauge, quadrupole mass spectrometer, sputter gun, annealing setup, etc.) a load lock system is available, which is evacuated by its own small turbo pump. The typical base pressure inside the chamber is at the limit of detectability using our hot cathode nude ion gauge with unmodified factory calibration (i.e. the vacuum is better than nominal $4*10^{-11}$ torr).

The deposition of organic material with a melting point close or above ambient temperature is a non-trivial task due to contamination of commercial available reactants with solvent residue in the percent range. Due to the relatively high gas pressure of these materials, they cannot be evaporated from inside the chamber, as during bake-out of the system they would be lost. Dosing through a leak valve requires significant effort in the purification and evaporation of the reactant in order not to enrich contaminants in the dosed portion of the reactant. This is, apart from the actual STM measurements, the experimentally most difficult and time-consuming part of the present scientific endeavor. Considerable effort was placed in the optimization of the dosing setup. It has to be mentioned that for STM measurements significant smaller coverages are required as for most other surface-science measurements. This puts additional pressure on the purity of the deposited portion as at no time volatile adsorbates such as CO or H_20 will be displaced by the chosen organic adsorbates.

Development of the Control Electronics





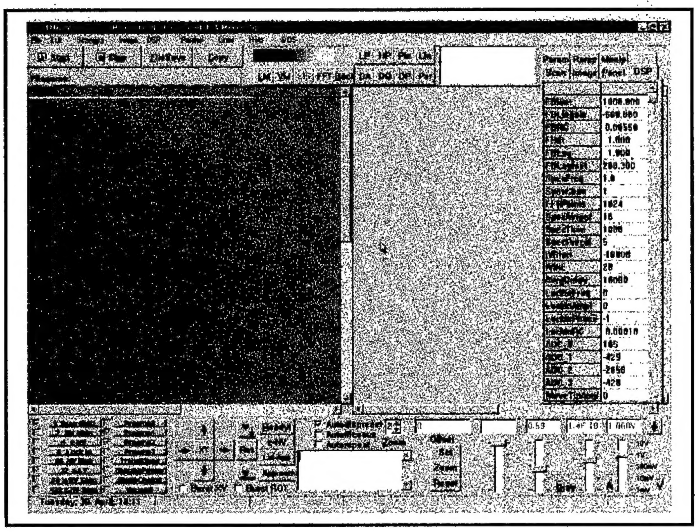


Between the signal processor and the STM an amplifier and signal converter (ASC) is placed. It separates the computer ground from the STM setup, thereby avoiding problems induced by the high-frequency signals within the computer. Commercial instrumentation amplifiers (Burr Brown) are used for this purpose. The piezoelectric tube scanners of this setup require bipolar contacts for scanning normal to their main axis. These are generated in the ASC from the x and y signals supplied by the DSP board. Finally, the ASC provides high-voltage operational amplifiers (Apex) capable of amplifying the signal to up to 250V of either polarity. This is needed for large scan ranges to survey the sample surface and, especially, for the coarse approach of the tip to the sample in a stick-and-slip fashion. The DSP board provides numerous digital signals, additionally. These are also transferred to the ASC. After ground conversion with opto-couplers, they are used for purposes like: setting the amplification of the x, y and z signals thereby choosing the resolution and scan range; control of the coarse approach

and modification of the amplification range of the preamplifier; etc. are also accomplished.

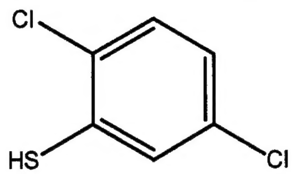
On the previous page the schematics of an ASC, the routing of its metallization layers and a computer-generated view of the actual main board can be seen. Detailed drawings and schematics can be submitted on request and in electronic format.

Adaptation of the Control Software

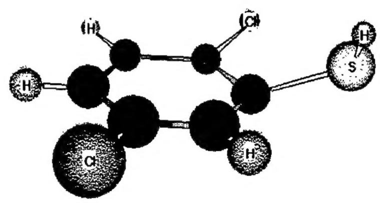


The control software of the DSP board is written in C and converted into machine code using software packages from Texas Instruments and Innovative Integration. The majority of the necessary code is already available from previous STMs of the PI. The board is housed in a conventional PC running Windows 95 (more recent versions of Windows provide problems with direct memory access). Dual ported memory is used for the data transfer between the PC and the signal processor. Controls signals are passed by a dedicated semaphore structure, which is hardware supported by the DSP board. STM measurements are initiated and controlled by the operator using a home-written, Windows-based user interface, of which the backbone is available and proven by use in various instruments in several German, Swedish and US universities. It is written in Delphi (Borland) and offers a typical Windows-style look, which permits the control of all scanning parameters and other data-acquisition tasks. Special attention is put on easy and intuitive software in order to reduce training time and to help users of the instrument to a quick start. A screen shot of the present user interface is shown on the left. Further image processing routines for tasks like automatic drift correction in sequences of images and automatic image recognition for molecule tracking are implemented in a home-written software package using IDL (Research Systems/Kodak) as programming language.

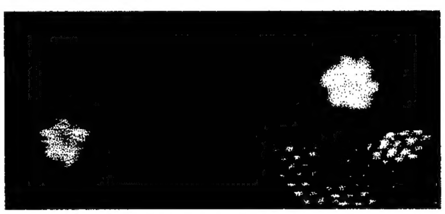
Current Investigations and Initial Results



2,5 dichlorothiophenol

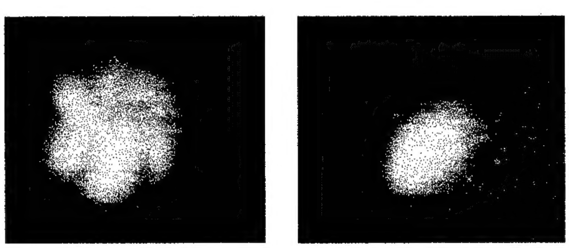


Current investigations focus on the elucidation of abstraction processes on heterosubstituted aromatic molecules. Generally, the controlled addressal of individual functional groups is the most important and basic step of chemistry. It is crucial for the setup of complex molecules from a variety of reactants. Presently, experiments conducted on the new setup use 2,5 dichloro-thio-phenol (DTP).



Two DTP molecules on Cu(111) at 13K. Two surface orientations of the molecule are apparent. The insert shows the atomic setup of the surface to scale. The insert was acquired using a different set of tunneling parameters.

At 10 K, DTP is found to be adsorbed on the surface in a flat geometry. The surface interaction is strongest for the sulfur atom causing the molecule to realign itself under the tip during scanning. Substrate interaction are strong enough, however, that only orientations in registry with the substrate's sixfold symmetry are found. Consequently, STM images of the molecules show a sixmembered ring at whose center the sulfur atom is located and around which the phenol ring rotates like horse on a peg.



DTP before and after activation with 500 mV electrons from the STM tip. The activated molecule experiences stronger adsorbated interactions and, hence, does not rotate under the tip.

Adsorption of the molecule on a metal surface reduces its available degrees of freedom, inversion with respect to the surface normal is forbidden. Hence two different stereoisomers of the molecule-substrate-complex exist: one with the para-chlorine in clockwise direction next to the sulfur and one in counter clockwise direction.

Subsequent activation of the molecule with 500 meV electrons results in stronger substrate bond which prevents rotation. Consequently, the molecule is only imaged in one surface orientation. Presently, the PI prepares publications of these findings. Thus activated molecules appear to be movable with the STM tip and experiments aiming at subsequent reactions are under way.